

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau(43) International Publication Date  
25 March 2004 (25.03.2004)

PCT

(10) International Publication Number  
WO 2004/025128 A1(51) International Patent Classification<sup>7</sup>: F15C 5/00(21) International Application Number:  
PCT/JP2003/011429(22) International Filing Date:  
8 September 2003 (08.09.2003)

(25) Filing Language: English

(26) Publication Language: English

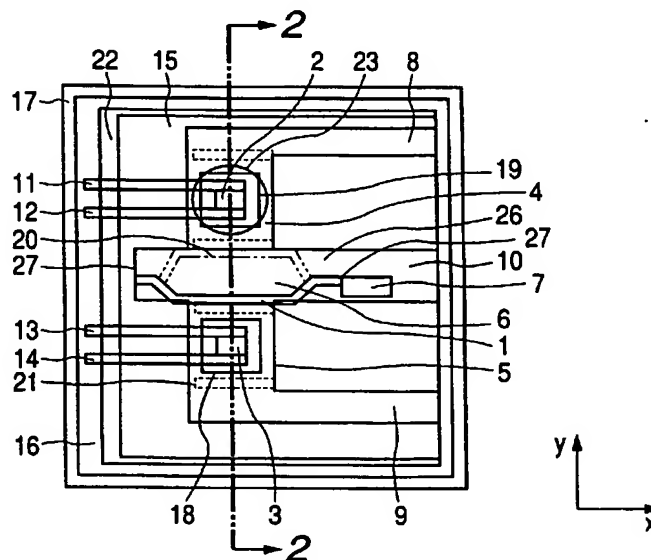
(30) Priority Data:  
NO. 2002-264676  
10 September 2002 (10.09.2002) JP  
NO. 2003-309901  
2 September 2003 (02.09.2003) JP(71) Applicant (for all designated States except US): CANON  
KABUSHIKI KAISHA [JP/JP]; 3-30-2, Shimomaruko,  
Ohta-ku, Tokyo 146-8501 (JP).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SUGIOKA,  
Hideyuki [JP/JP]; c/o CANON KABUSHIKI KAISHA,3-30-2, Shimomaruko, Ohta-ku, Tokyo 146-8501 (JP).  
YAMAZAKI, Takeo [JP/JP]; c/o CANON KABUSHIKI  
KAISHA, 3-30-2, Shimomaruko, Ohta-ku, Tokyo  
146-8501 (JP).(74) Agents: OKABE, Masao et al.; No. 602, Fuji Bldg., 2-3,  
Marunouchi 3-chome, Chiyoda-ku, Tokyo 100-0005 (JP).(81) Designated States (national): AE, AG, AL, AM, AT, AU,  
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,  
CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE,  
GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ,  
LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN,  
MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO,  
RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT,  
TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.(84) Designated States (regional): ARIPO patent (GH, GM,  
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),  
European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE,  
ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO,  
SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM,  
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: LIQUID DELIVERY DEVICE



(57) Abstract: A liquid delivery device comprises a flow channel (10) for flowing a liquid, at least two pressure-generating means (2,3) for generating pressures provided in the flow channel, and a variable member (1) placed between the pressure-generating means and capable of transforming between a first stable state and a second stable state by a generated pressure; the device serving to select a branch of the flow channel by transforming the variable member into the first stable state or the second stable state. A valve for changeover of flow channel branches comprises a variable member placed between pressure-generating means and transformable between a first stable state and a second stable state by a generated pressure, the valve serving to select a branch of flow channel branches by the variable member.

WO 2004/025128 A1



**Published:**

— with international search report

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

## DESCRIPTION

## LIQUID DELIVERY DEVICE

## 5 TECHNICAL FIELD

The present invention relates to a liquid delivery device. Specifically, the present invention relates to a liquid delivery device which is useful for delivery of a micro quantity of a liquid in  
10 chemical analysis apparatuses, medical apparatuses, biotechnology apparatuses, ink-jet printing systems, and the like; particularly to a micro-valve useful for microanalysis systems ( $\mu$ TAS: Micro Total Analysis Systems) for conducting chemical analysis or chemical  
15 synthesis on a chip, ink delivery systems of ink-jet printers, and the like systems.

## BACKGROUND ART

In recent years with development of three-  
20 dimensional fine processing techniques, the systems attracting attention are those which comprise fluid elements such as a fine flow path, a pump, and a valve, and a sensor integrated on a substrate like glass or silicon, and conduct chemical analysis on  
25 the substrate. Such a system is called a microanalysis system, a  $\mu$ -TAS (Micro Total Analysis System), or Lab on a Chip. The miniaturization of

the chemical analysis system enables decrease of an ineffective space volume and remarkable decrease of the sample size.

The miniaturization enables also shortening of  
5 the analysis time and decrease of power consumption of the entire system. Further, the miniaturization is promising for lowering the price of the system. Furthermore, the  $\mu$ -TAS is promising in medical services such as home medical care and bed-side  
10 monitoring, and biological chemical techniques such as geonomics analysis and proteomics analysis.

Japanese Patent Application Laid-Open No. 10-337173 discloses a micro-reactor for conducting a sequence of biochemical experiment steps comprising  
15 mixing solutions to cause reaction, analyzing quantitatively the reaction product, and separating the product, by using combination of cells. Fig. 17 illustrates schematically a concept of micro-reactor 501. Micro-reactor 501 has an isolated reaction  
20 chamber closed tightly with a flat plate on a silicon substrate. This micro-reactor has reservoir cell 502, mixing cell 503, reaction cell 504, detection cell 505, and separation cell 506 in combination. By providing such a reactor in plurality on a substrate,  
25 many biochemical reactions can be allowed to proceed simultaneously concurrently. Not only the analysis, but material synthesis such as protein synthesis can

be conducted in the cells.

Japanese Patent Application Laid-Open No. 5-1669 discloses a valve employing a diaphragm, and a micro-pump utilizing the valve and a piezo element.

5 U.S. Patent 6533400 discloses an ink-jet head employing a valve constituted of a movable member (cantilever).

Jr-Hung Tasai and Liwei Lin: "A Thermal Bubble Actuated Micro Nozzle-Diffuser Pump", Proceedings of  
10 the 14th, IEEE International Conference on Micro Electro Mechanical Systems, 2001, pp.409-412.  
discloses a valveless micro-pump utilizing a liquid-control function of a bubble generated by heating of the liquid and a nozzle type diffusion element.

15 Jong Soo Ko, et al.: Appl. Phys. Lett. Vol.81, No.3, July 15, 2002, pp.547-549 discloses an optical switch employing an actuator utilizing interaction of a magnetic field and an electric current.

Jin Qiu, et al.: "Proceedings of MEMS 2001",  
20 2001, pp.353-356 mentions usefulness of mechanical bistability for relays and valves.

However, conventional micro-valves employing a diaphragm or a cantilever require external force to keep the valve opened or closed as desired.

25 On the other hand, the mechanically bistable element needs extra driving force for transformation between the two stable structures owing to a high

potential energy barrier between the two structures in comparison with an element having no mechanical bistability.

Generally the lower potential energy barrier  
5 between the two structures for decreasing the  
aforementioned extra driving force will make instable  
the retention of the stable states.

#### DISCLOSURE OF THE INVENTION

10 The present invention has been accomplished in  
view of the aforementioned prior art techniques, and  
intends to provide a liquid delivery device which is  
capable of retaining a valve in a closed state or an  
opened state without applying external force for the  
15 retention of the state.

According to an aspect of the present invention,  
there is provided a liquid delivery device,  
comprising: a flow channel for flowing a liquid,  
at least two pressure-generating means for generating  
20 pressures provided in the flow channel, and  
a variable member placed between the pressure-  
generating means and capable of transforming between  
a first stable state and a second stable state by a  
generated pressure; the device serving to select a  
25 branch of the flow channel by transforming the  
variable member into the first stable state or the  
second stable state.

According to another aspect of the present invention, there is provided a valve for changeover of flow channel branches, comprising a variable member placed between pressure-generating means and  
5 transformable between a first stable state and a second stable state by a generated pressure, the valve serving to select a branch of flow channel branches by the variable member.

Thus, the present invention provides a liquid  
10 delivery device which is capable of retaining the flow channel in a closed state or an opened state arbitrarily, without applying external force, owing to use of the variable member as flow channel-controlling means for closing or opening the flow  
15 channel, the variable member being transformable between the first stable state and the second stable state.

#### BRIEF DESCRIPTION OF THE DRAWINGS

20 Fig. 1 illustrates schematically a liquid delivery device of a first embodiment of the present invention.

Fig. 2 is a sectional view of the device of the first embodiment of Fig. 1 taken along line 2-2 in  
25 Fig. 1.

Fig. 3 illustrates schematically a steric structure of variable member 1 having a deflected

structure of an embodiment of the liquid delivery device of the present invention.

Figs. 4A and 4B illustrate schematically variable member 1 in a gently deflected structure.

5 Figs. 5A and 5B illustrate schematically basic function of the first embodiment of the liquid delivery device of the present invention.

Figs. 6A and 6B illustrate schematically the function of selecting the flow channel branches in  
10 the first embodiment of the liquid delivery device of the present invention.

Fig. 7 illustrates schematically a second embodiment of the liquid delivery device of the present invention.

15 Fig. 8 illustrates schematically a third embodiment of the liquid delivery device of the present invention.

Figs. 9A and 9B illustrate schematically a first basic function of the third embodiment of the  
20 liquid delivery device of the present invention.

Figs. 10A and 10B illustrate schematically a second basic function of the third embodiment of the liquid delivery device of the present invention.

Figs. 11A and 11B illustrate schematically the  
25 function of switching the flow channel branches in the third embodiment of the liquid delivery device of the present invention.

Fig. 12 illustrates schematically a fourth embodiment of the liquid delivery device of the present invention.

Fig. 13 illustrates schematically a fifth  
5 embodiment of the liquid delivery device of the present invention.

Figs. 14A and 14B illustrate schematically the function of switching the flow channel in the fifth embodiment of the liquid delivery device of the  
10 present invention.

Fig. 15 illustrates schematically a sixth embodiment of the liquid delivery device of the present invention.

Fig. 16 illustrates schematically a seventh  
15 embodiment of the liquid delivery device of the present invention.

Fig. 17 illustrates schematically a conventional micro-reactor.

Fig. 18 illustrates schematically an eighth  
20 embodiment of the liquid delivery device of the present invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

Preferred embodiments of the present invention  
25 are shown below.

The variable member is preferably the liquid delivery device, wherein the variable member is

comprised of a flexible resin film, and more preferably comprised of plural flexible resin films linked in tern.

The variable member is comprised of an arch-shaped elastic body, and expandable elastic bodies  
5 placed on both ends of the arch-shaped elastic body.

The liquid delivery device of the present invention may comprise further a magnetic field-generating means for generating a magnetic field, and  
10 the variable member has a means for promoting transformation between the first stable state and the second stable state by the generated magnetic field.

The liquid flow channel is comprised of a first flow channel branch and a second flow channel branch  
15 provided with the pressure generating means, and a third flow channel branch is connected to the first flow channel branch and the second flow channel branch, and either the first flow path branch or the second flow channel branch is closed by the variable  
20 member.

The liquid delivery device of the present invention preferably comprises further a waste liquid reservoir for receiving a waste liquid from the flow channel, and the waste liquid is introduced into the  
25 waste liquid reservoir by selecting the stable state of the variable member. In this case, more preferably, the liquid delivery device comprises

further an analysis column for analyzing the liquid,  
and a pressurizing liquid terminal for introducing  
the liquid into the analysis column, and the liquid  
is introduced either into the waste liquid reservoir  
5 or into the analysis column by selecting the stable  
state of the variable member.

In the pressure-generating means of the present  
invention, the liquid delivery device may be a heater,  
and the flow channel branch is changed over by growth  
10 and contraction of a bubble formed by the heater.

<EXAMPLES>

Embodiments of the present invention are  
explained below in more detail by reference to  
Examples.

15 (First Embodiment)

Fig. 1 illustrates a first embodiment of the  
liquid delivery device of the present invention.  
Numeral 1 denotes a variable member transformable  
between a first stable state and a second stable  
20 state, the variable member being shown in one stable  
state in the drawing. The other numerals denote the  
following: 2 and 3, respectively a heater for bubble  
formation; 4 and 5, respectively a bubbling chamber;  
6, a variable member-retaining chamber; 7, a  
25 supporting stand for the variable member; 8 to 10,  
respectively a flow channel branch; 11 to 14,  
respectively an electrode; 15, a resin film for

comprising the flow channel; 22, an insulating SiN layer of 0.3  $\mu\text{m}$  thick; 16, a heat-reserving  $\text{SiO}_2$  layer of 2.7  $\mu\text{m}$  thick; 17, an Si substrate of 0.67 mm thick; 18 and 19, respectively a Ta thin film of 0.2  $\mu\text{m}$  thick; 20, the position of the other stable state of variable member 1; 21, an adjusting wall for adjusting the inertance before and after the bubbling chamber and adjusting the inlet aperture size; 23, a bubble generated by heater 2; 27, a supporting portion for variable member 1; and 26, a channel-closing member for opening and closing the flow channel by employing the variable member transformable between the first stable state and the second stable state.

15 In other words, in this embodiment, a micro-valve as a liquid delivery device is provided which comprises flow channel branches 8-10, variable member 1 transformable between the first stable state and the second stable state, and heaters 2 and 3, and is capable of opening and closing the flow channel by transformation of variable member 1 between the first stable state and the second stable state by utilizing growth or contraction of bubbles generated by the heaters, and is retainable arbitrarily in the closed state or the open state without continuing to add an external force for the retention.

The embodiment may be characterized in that

variable member 1 is a flexible resin film in a deflected structure. In this embodiment, the flow channel may be also made of the resin film. In this case, the flow channel and the variable member can be  
5 formed effectively in integration by photolithography.

With a simple elastic body, in one method for stabilizing the elastic body equally in the first stable state and the second stable state, a straight flat spring without stress is prepared and deflected.  
10 The same level of stability can be obtained by photolithography by utilizing difference in thermal expansion coefficient. However, such a deflected structure at the preparing step, which is referred to as a first stable state in this discussion, is in the  
15 most stable state, and a second stable state is a metastable state having a higher energy than the first stable state, being possibly insufficient in the stability. When a resin film having viscoelasticity in a deflected structure is employed  
20 as the variable member, such a viscoelastic variable member exhibits an elastic response to an instant external force to retain each of the stable and metastable states, and if any one of the states is held for relative long time, the member causes a  
25 viscous flow so that a shape under the state held is more stable. Accordingly, in this embodiment, a viscoelastic resin film in a flexible structure is

preferably employed as the variable member because the metastable state will become stabilized with lapse of time to give a valve of high stability against external disturbance advantageously.

5           The above-mentioned viscoelastic effects of the resin are made more remarkable preferably by heating the liquid for bubble formation.

          The material of the resin film includes cured cation-polymerized epoxy resins; methacrylate ester  
10   resins formed from methyl methacrylate, ethyl methacrylate and the like; polymethacrylonitrile; poly- $\alpha$ -methylstyrene; cellulose acetate; polyisobutylene; polymethyl isobutyl ketone; and polymethacrylamide.

15           This embodiment is characterized also in that a pair of heaters 1 and 2 are respectively placed on each side of variable member 1 and the state of the variable member can be transformed between the first stable state and the second stable state by bubbling  
20   caused by the pair of heaters.

          The device of this embodiment provides a three-way valve which comprises a first flow channel branch 8, a second flow channel branch 9, and a third flow channel branch 10, and a variable member-holding room  
25   6 containing variable member 1 and connecting the three flow channel branches, a first heater 2 placed in the first channel branch 8, and a second heater 3

placed in the second channel branch 9. Thereby,  
variable member 1 is transformed by bubbling caused  
by first heater 2 or second heater 3 between the  
first stable state and the second stable state to  
5 close first channel branch 8 or second channel branch  
9. Thus the three-way valve has function (1) to  
introduce the liquid introduced from third channel  
branch 10 into first channel branch 8 or second  
channel branch 9, or (2) to introduce selectively the  
10 liquid from first channel branch 8 or the liquid from  
second channel branch 9 into third channel branch 10.

Fig. 2 is a sectional view of the device of the  
first embodiment of Fig. 1 taken along line 2-2 in  
Fig. 1. In Fig. 2, the numerals denote the  
15 following: 24, a first stable state of variable  
member 1; 25, a second stable state of variable  
member 1; 21A to 21D, respectively an adjusting wall  
for adjusting the inertance before and after the  
bubbling chamber and for adjusting the inlet aperture  
20 size. Bubbling chambers 4 and 5 and variable member-  
holding room 6, which also function actually as the  
flow channel, have respectively a height of 30  $\mu\text{m}$ ,  
and a breadth of 30  $\mu\text{m}$ . Adjusting walls 21A to 21D  
have respectively a height of 10  $\mu\text{m}$ . The inlet  
25 apertures of adjusting walls 21B and 21C have  
respectively a breadth of 10  $\mu\text{m}$  in the height  
direction (z direction). Variable member 1 has a

breadth of 20  $\mu\text{m}$  in the height direction (z direction). Variable member 1 has a thickness of 5  $\mu\text{m}$  in the y direction. The distance between portions 27 for supporting the variable member is 200  $\mu\text{m}$ .

5           With such a structure, heating of the liquid by heater 2 brings variable member 1 to a first stable state as shown by numeral 24 in which state the variable member 1 is in contact with adjusting wall 21C for adjusting the size of the inlet aperture.

10           Fig. 3 illustrates schematically a steric structure of variable member 1 having a deflected structure of this embodiment. In Fig. 3, deflectable portion 32 longer than the distance 31 between supporting portions 27 for the variable member is  
15 kept at a first stable state or a second stable state at the positions nearly symmetrical as shown by numerals 1 and 20 in Fig. 1 with respect to the line connecting the supporting portions 27.

          Figs. 4A and 4B illustrate schematically the  
20 variable member in a gently deflected structure. This deflection structure may be formed with gentle deflection so as to be supported by supporting portions 27 on the both side with respect to the center line 41 as shown in Fig. 4A. In this case  
25 also, a stable state can be obtained, when the variable member is pressed against wall 42 having inlet aperture 43, to close the flow channel with

complicated deformation of the variable member as shown in Fig. 4B. Such a closing state is also shown schematically with simplification as shown by numeral 44.

5        Figs. 5A and 5B illustrate schematically basic operation of the first embodiment of the liquid delivery device of the present invention. Figs. 5A and 5B shows operation of a micro-valve of this embodiment in which a liquid is allowed to bubble by  
10    heating by application of voltage to heating resistor 2. In Fig. 5A, variable member 1 in a first stable state is transformed into second stable state 24 by bubble formation at a high pressure of about 100 atm and bubble growth to cross a potential barrier to the  
15    variable member transformation to open first flow channel branch 8 and close second flow channel branch 9. In Fig. 5B shows the state of bubble contraction. In Fig. 5B, variable member 1 in the second stable state 24 tends to return to the first stable state  
20    owing to the contraction of the bubble. However, variable member 1 is retained in the second stable state, since there is a potential barrier corresponding to the stabilization energy for transformation of the variable member to be crossed  
25    between the first stable state and the second stable state and the pressure difference in the contraction is about 1 atm or less, much smaller than the

pressure difference of bubbling.

In this embodiment, third channel branch 10 is formed in a direction parallel to variable member 1, whereby the variable member is less affected by the flow during contraction of the bubble, advantageously.

Figs. 6A and 6B illustrate schematically the function of changing over the flow channel branches in the first embodiment of the present invention. Figs. 6A and 6B shows the function of changeover of the flow channel branches realized by a micro-valve of this embodiment. Fig. 6A shows flow route 61 of the liquid introduced through third channel branch 10 and fed to first flow channel branch 8. Fig. 6B shows flow route 62 of liquid introduced through third channel branch 10 and fed to second channel branch 9. Otherwise, the reverse flow direction of routes 61 and 62 can be utilized as a two-input/one-output type of liquid changeover element.

In this embodiment, heating resistors 2 and 3 are thin TaN films of 0.05  $\mu\text{m}$  thick, and the heating body has a size of 25  $\mu\text{m}$   $\times$  25  $\mu\text{m}$  and has a resistance of 53  $\Omega$ . The variable member is transformed by a rectangular pulse of 8 V, 1  $\mu\text{s}$  between the stable states.

(Second Embodiment)

Fig. 7 illustrates schematically a second embodiment of the liquid delivery device of the

present invention. Fig. 7 shows the feature of the second embodiment. This embodiment is nearly the same as the first embodiment except that the variable member is constituted of plural deflectable resin  
5 films 74 and 75 linked by linking films 71, 72 73.

The variable member constructed of viscoelastic resin films linked by linking films can realize a stable valve for tight closure.

The material for the resin film includes cured  
10 cation-polymerized epoxy resins; methacrylate ester resins formed from methyl methacrylate, ethyl methacrylate and the like; polymethacrylonitrile; poly- $\alpha$ -methylstyrene; cellulose acetate; polyisobutylene; polymethyl isobutyl ketone; and  
15 polymethacrylamide.

(Third Embodiment)

Fig. 8 illustrates schematically a third embodiment of the liquid delivery device of the present invention. Fig. 8 shows the feature of the  
20 third embodiment. This embodiment is nearly the same as the first embodiment except that the device comprises first flow channel branch 81, second flow channel branch 82, third flow channel branch 83, variable member-holding room 84 which holds the  
25 variable member 1 and connects the above three flow channel branches together, and a pair of heaters 2 and 3 placed on each side of the variable member; and

the first flow branch is closed and opened with the variable member by bubbling caused by the pair of heaters.

In this embodiment, bubbling caused by heater 2  
5 brings variable member 1 into the second stable state to open inlet 91 as shown in Figs. 9A and 9B, whereas bubbling caused by heater 3 brings variable member 1 into the first stable state to close inlet 91 as shown in Figs. 10A and 10B.

10 The valve of this embodiment opens and closes selectively only specific one of the three flow channel branches as shown in Figs. 11A and 11B.

(Fourth Embodiment)

Fig. 12 illustrates schematically a fourth  
15 embodiment of the liquid delivery device of the present invention. This embodiment, as shown in Fig. 12, is nearly the same as the first embodiment and the third embodiment except that the device comprises sample room 121, first waste liquid reservoir 122,  
20 second waste liquid reservoir 123, pressurizing liquid terminal 124, analysis column connecting terminal 138, a flow channel, and variable members 128, 129 and 130; and routes (a), (b) and (c) below are formed by changeover of the variable member:  
25 (a) a route for flow of the liquid from the sample room to the first waste liquid reservoir,  
(b) a route for flow of the liquid from the sample

room to the second waste liquid reservoir, and  
(c) a route for flow of the liquid from the sample  
room to the analysis column-connecting terminal.

Here the "waste liquid" includes a liquid  
5 having been used for washing of the flow channel, and  
like liquids. That is, the waste liquid having used  
for flow channel washing is sent to the waste liquid  
reservoir. In this example, two waste liquid  
reservoirs are provided, but the reservoir is not  
10 limited thereto.

In Fig. 12, numeral 126 denotes a sample room,  
for example, for promoting initiation of production  
of protein, and numeral 127 denotes a sample room for  
storing a solution for dissolving the protein. A  
15 solution containing a protein to be analyzed is sent  
out from sample room 121 to the analysis column 125  
for the analysis.

The terminal for pressurization is used for  
introducing a liquid into the analysis column. The  
20 liquid is introduced into the analysis column by  
application of a pressure.

(Fifth Embodiment)

Fig. 13 illustrates schematically a fifth  
embodiment of the liquid delivery device of the  
25 present invention. This embodiment, as shown in Fig.  
13, is nearly the same as the first embodiment and  
the third embodiment except that the device has a

flow channel, a pair of variable members 131 and 132 having respectively a first stable state and a second stable state, and a heater 133 between the pair of variable members for bubble formation, one variable member 131 functions to prevent a back flow to allow the liquid flow toward the heater only, and the other variable member 132 functions to prevent a back flow to allow the flow from the heater only.

Figs. 14A and 14B show the basic operation in the fifth embodiment of the liquid delivery device of the present invention. In this embodiment, as shown in Figs. 14A and 14B, the growing bubble brings variable member 131 into a stable state 131A to close the liquid inlet 134, and variable member 132 into a stable state 132A to open the liquid inlet 135. Thereby the liquid in bubbling chamber 137 is delivered in the direction 136.

The contraction of the bubble brings variable member 131 into a stable state 131B to open liquid inlet 134, and variable member 132 into a stable state of 132B to close liquid inlet 135. Thereby the liquid is introduced in direction 138 into bubbling chamber 137.

As described above the micro-valve of the second embodiment functions as a pump mechanism by utilizing the two flows 136 and 138.

(Sixth Embodiment)

Fig. 15 illustrates schematically a sixth embodiment of the liquid delivery device of the present invention. This embodiment, as shown in Fig. 15, is nearly the same as the first embodiment and the third embodiment except that the variable member is comprised of arch-shaped spring 151 and a pair of expansion springs 152, 153 on each side of the arch-shaped spring.

In this embodiment, the pair of expansion springs 152, 153 enables effective adjustment of the stability and the potential barrier.

(Seventh Embodiment)

Fig. 16 illustrates schematically a seventh embodiment of the liquid delivery device of the present invention. This embodiment, as shown in Fig. 16, is nearly the same as the first embodiment and the third embodiment except that the device has an electroconductive variable member and a magnetic field-generating means for generating magnetic field B, and an electric current flow  $i$  promotes the transformation between the first stable state and the second stable state.

In Fig. 16, the magnetic field is generated by a plate-shaped permanent magnet 164 composed of NdFeB with a magnetic flux density of 3000 G. On the bubble formation, application of electric current of about 700 mA to the variable member strengthen the

force of the bubble by Lorentz force to drive the variable member toward the first stable state or the second stable state.

The liquid delivery device of this invention is  
5 useful as a micro-valve for a micro total analysis system ( $\mu$ TAS) for conducting chemical analysis or chemical synthesis on a chip, and an ink feeding system in an ink-jet printer.

(Eighth Embodiment)

10 Fig. 18 shows features of eighth embodiment. The numerals denote the following: 175a, 175b, 177a, and 177b, respectively an electrode for applying a voltage to a piezo element; 176a and 176b, respectively a piezoelectric material layer; 171a and  
15 171b, respectively a piezoelectric element as the pressure-generating means.

This embodiment is the same as First Embodiment except that piezoelectric elements are used as the pressure-generating means.

## CLAIMS

1. A liquid delivery device, comprising:  
a flow channel for flowing a liquid,  
at least two pressure-generating means for generating  
5 pressures provided in the flow channel, and  
a variable member placed between the pressure-  
generating means and capable of transforming between  
a first stable state and a second stable state by a  
generated pressure;  
10 the device serving to select a branch of the flow  
channel by transforming the variable member into the  
first stable state or the second stable state.
2. The liquid delivery device according to  
15 claim 1, wherein the variable member is comprised of  
a flexible resin film.
3. The liquid delivery device according to  
claim 2, wherein the variable member is comprised of  
20 plural flexible resin films linked in tern.
4. The liquid delivery device according to  
claim 1, wherein the variable member is comprised of  
an arch-shaped elastic body, and expandable elastic  
25 bodies placed on both ends of the arch-shaped elastic  
body.

5. The liquid delivery device according to claim 1, wherein the device comprises further a magnetic field-generating means for generating a magnetic field, and the variable member has a means  
5 for promoting transformation between the first stable state and the second stable state by the generated magnetic field.

6. The liquid delivery device according to  
10 claim 1, wherein the flow channel is comprised of a first flow channel branch and a second flow channel branch provided with the pressure generating means, and a third flow channel branch is connected to the first flow channel branch and the second flow channel  
15 branch, and either the first flow path branch or the second flow channel branch is closed by the variable member.

7. The liquid delivery device according to  
20 claim 1, wherein the device comprises further a waste liquid reservoir for receiving a waste liquid from the flow channel, and the waste liquid is introduced into the waste liquid reservoir by selecting the stable state of the variable member.

25

8. The liquid delivery device according to claim 7, wherein the device comprises further an

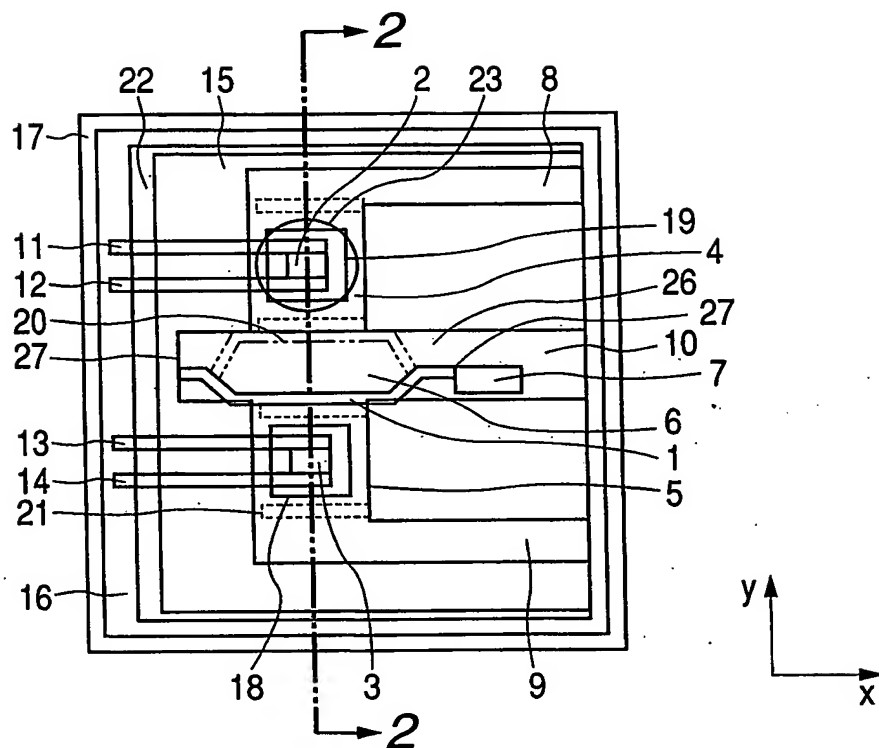
analysis column for analyzing the liquid, and a  
pressurizing liquid terminal for introducing the  
liquid into the analysis column, and the liquid is  
introduced either into the waste liquid reservoir or  
5 into the analysis column by selecting the stable  
state of the variable member.

9. The liquid delivery device according to  
claim 1, wherein the pressure-generating means is a  
10 heater, and the flow channel branch is changed over  
by growth and contraction of a bubble formed by the  
heater.

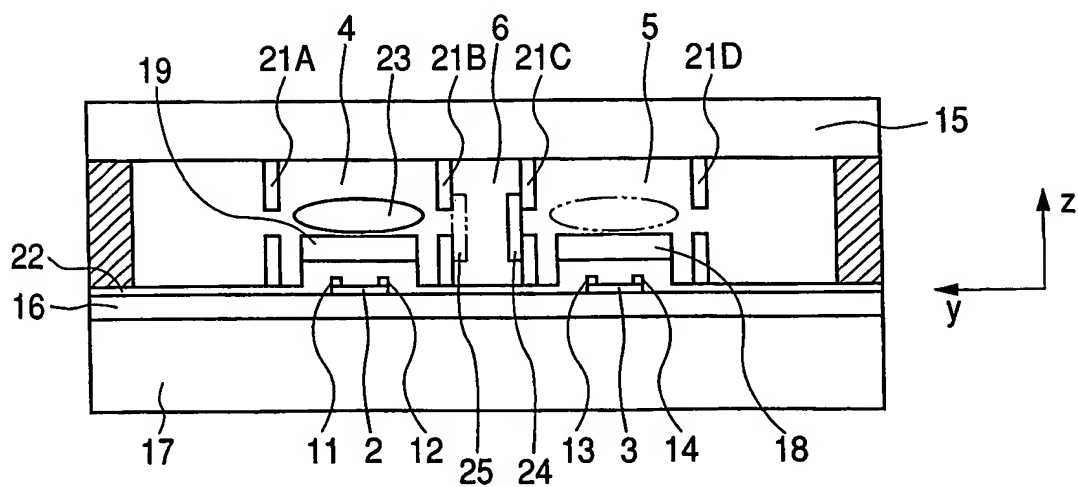
10. A valve for changeover of flow channel  
15 branches, comprising a variable member, said variable  
member being placed between pressure-generating means  
for generating a pressure provided in the flow  
channel such that the variable member is  
transformable between a first stable state and a  
20 second stable state by the generated pressure.

1 / 14

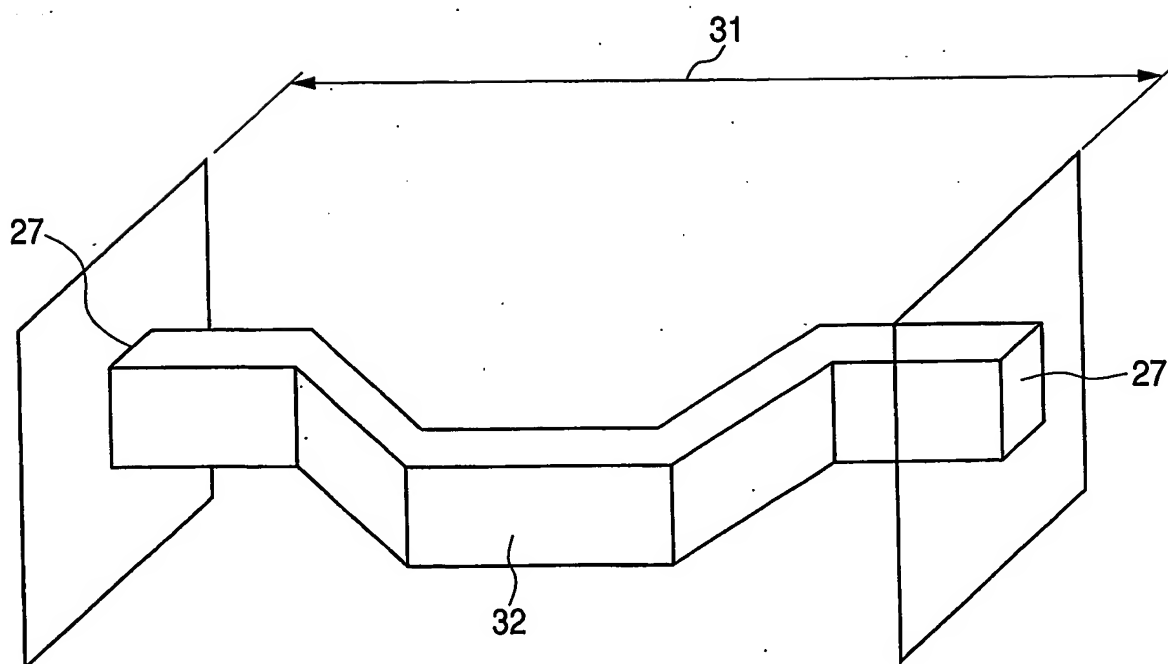
**FIG. 1**



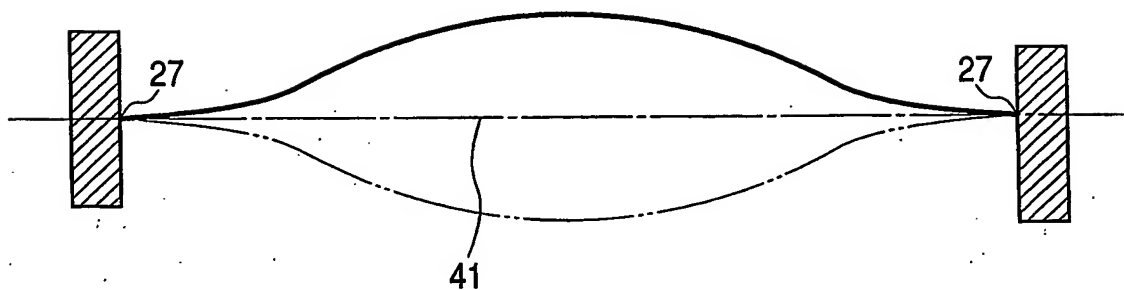
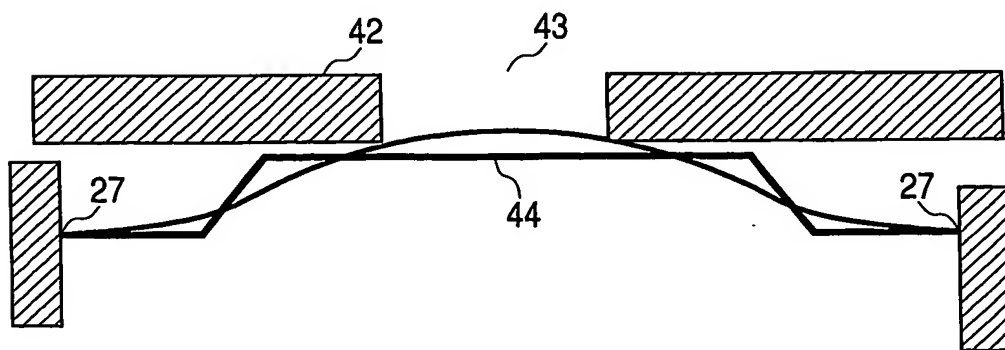
**FIG. 2**



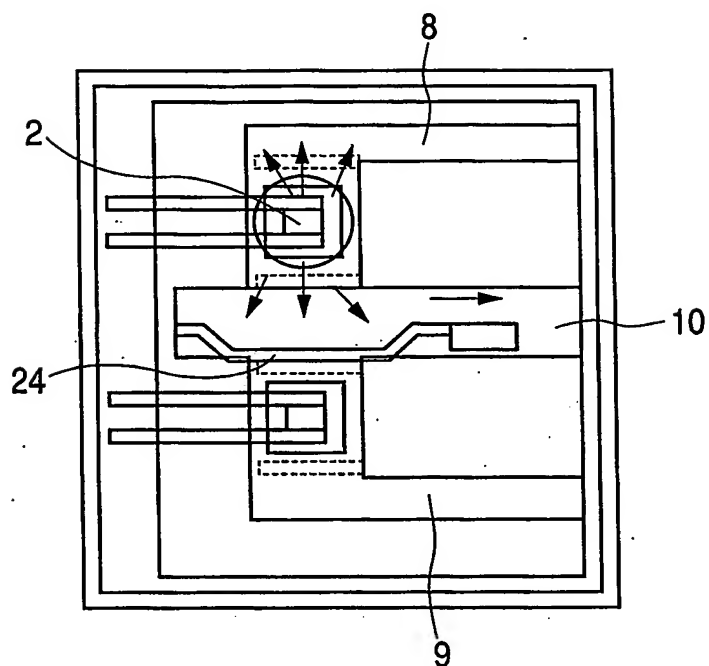
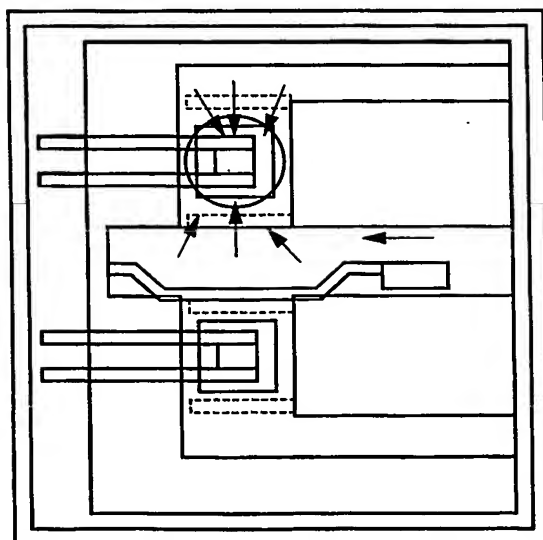
**FIG. 3**



3 / 14

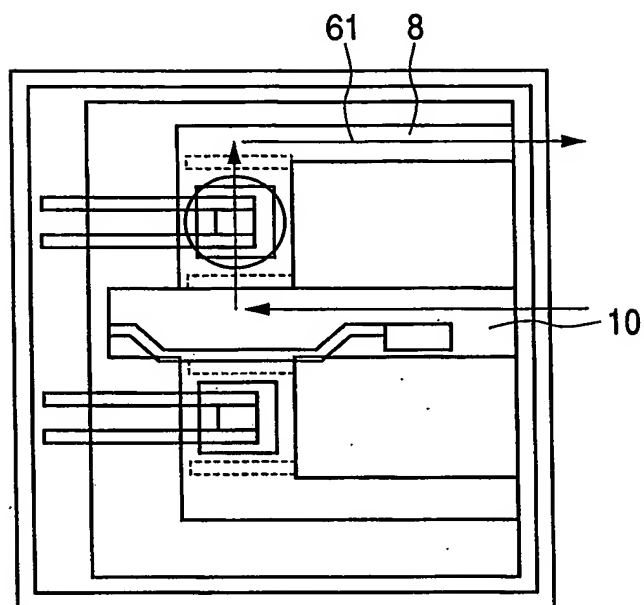
*FIG. 4A**FIG. 4B*

4 / 14

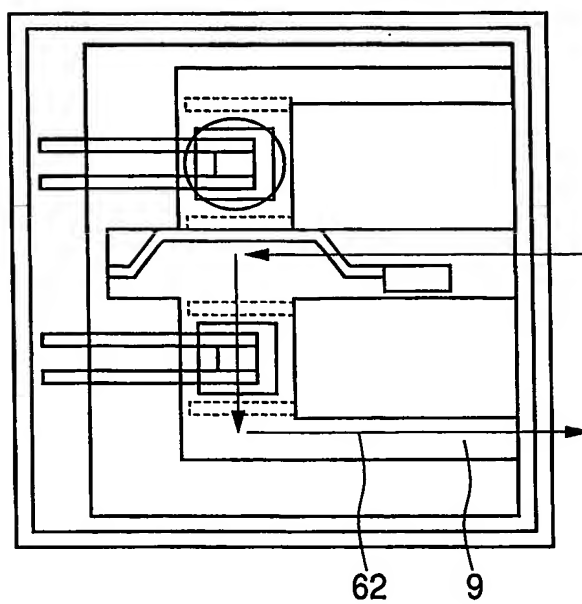
**FIG. 5A****FIG. 5B**

5 / 14

**FIG. 6A**

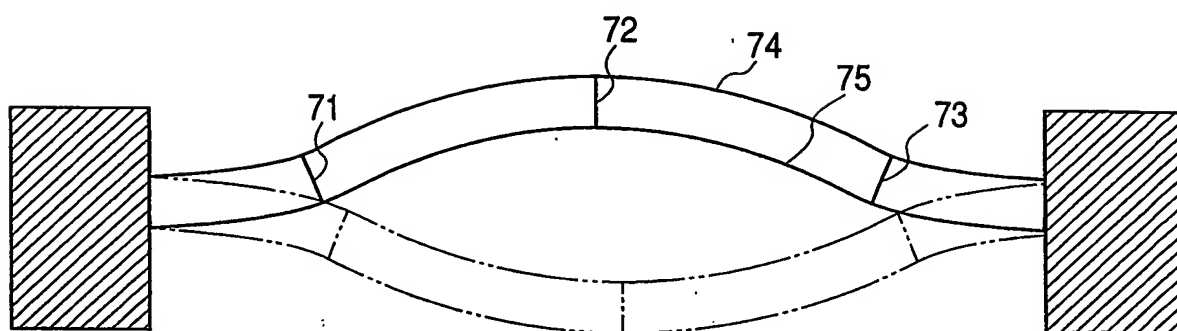


**FIG. 6B**

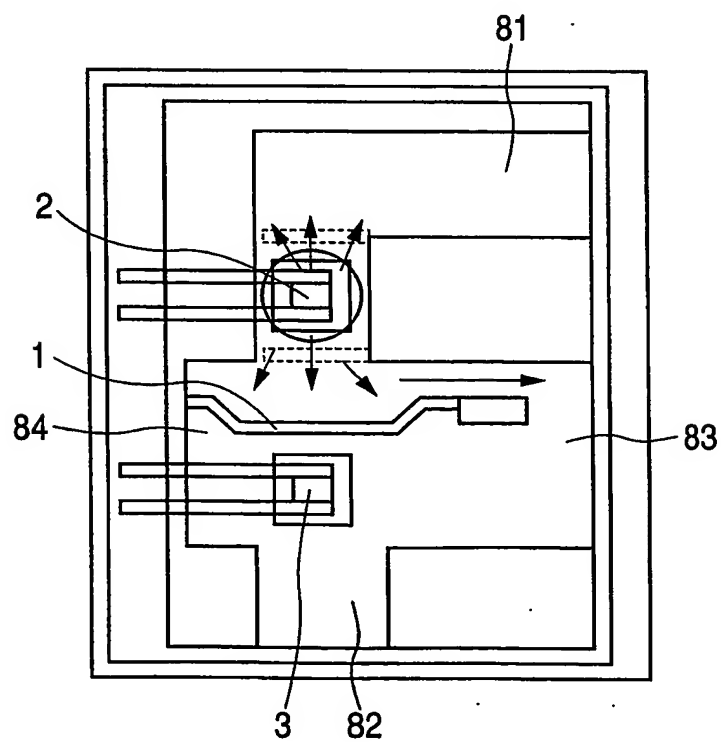


6 / 14

**FIG. 7**

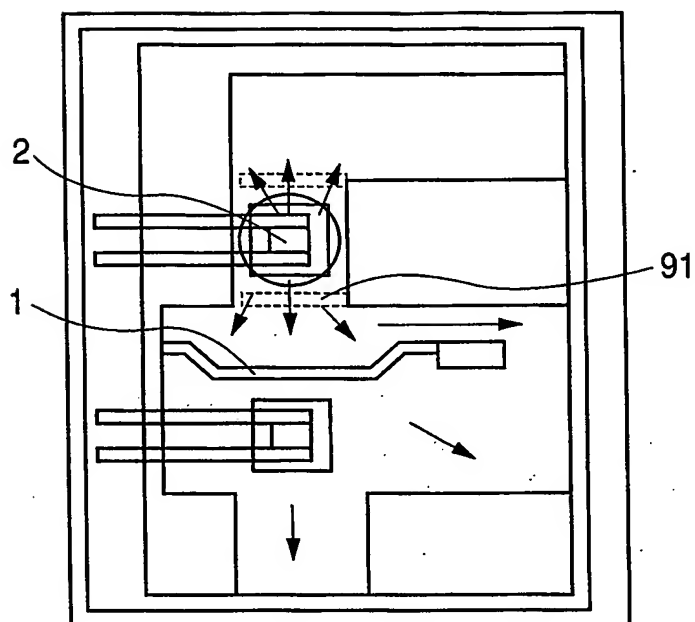


**FIG. 8**

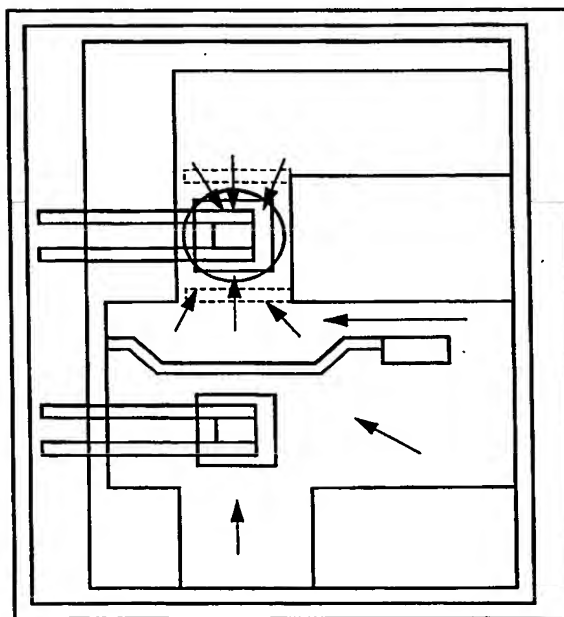


7/14

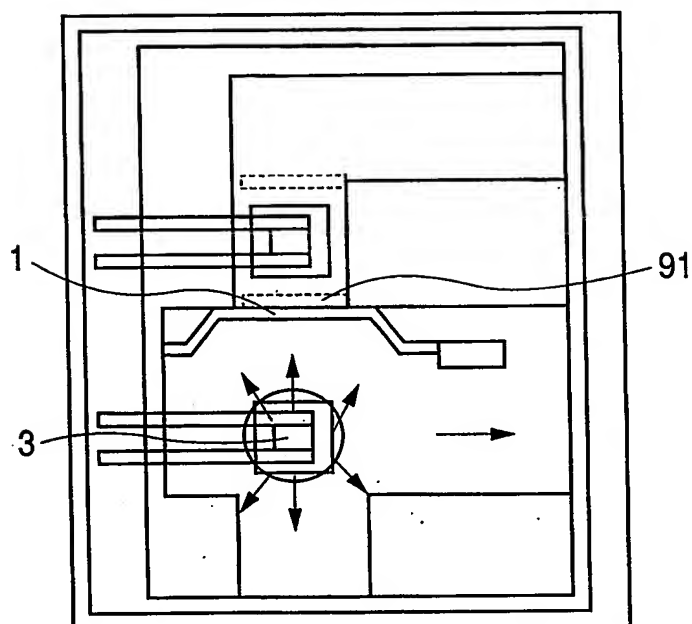
**FIG. 9A**



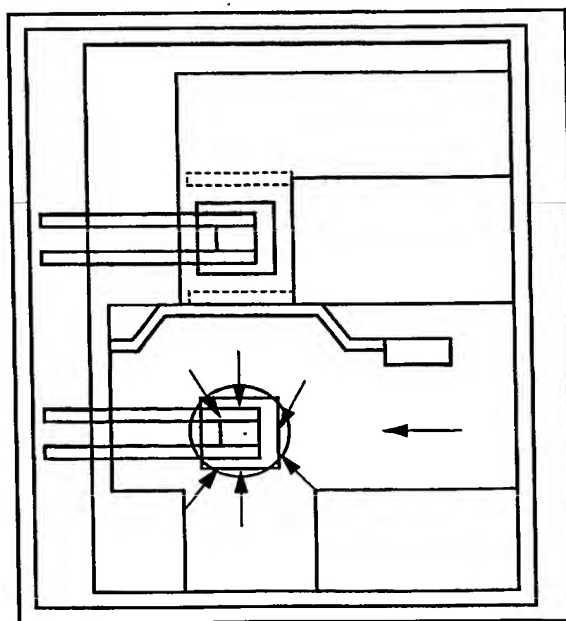
**FIG. 9B**



**FIG. 10A**

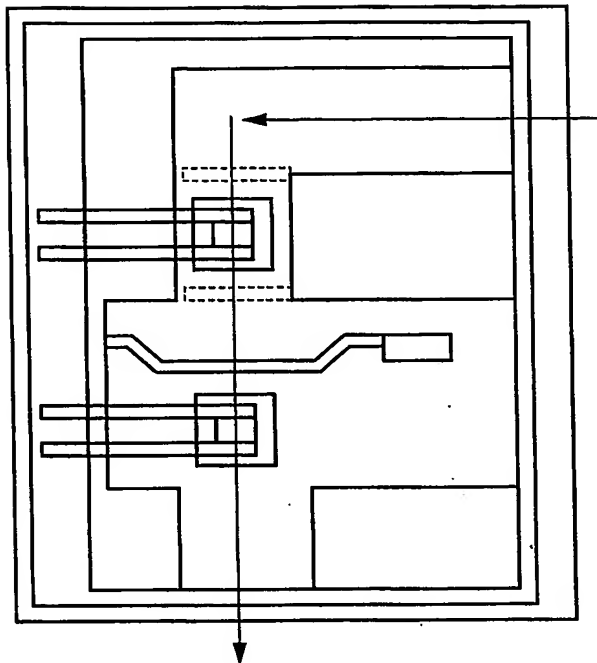


**FIG. 10B**

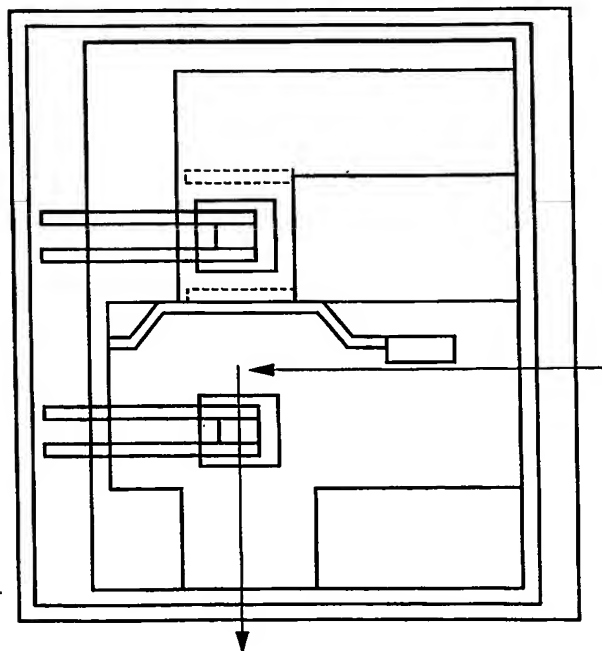


9 / 14

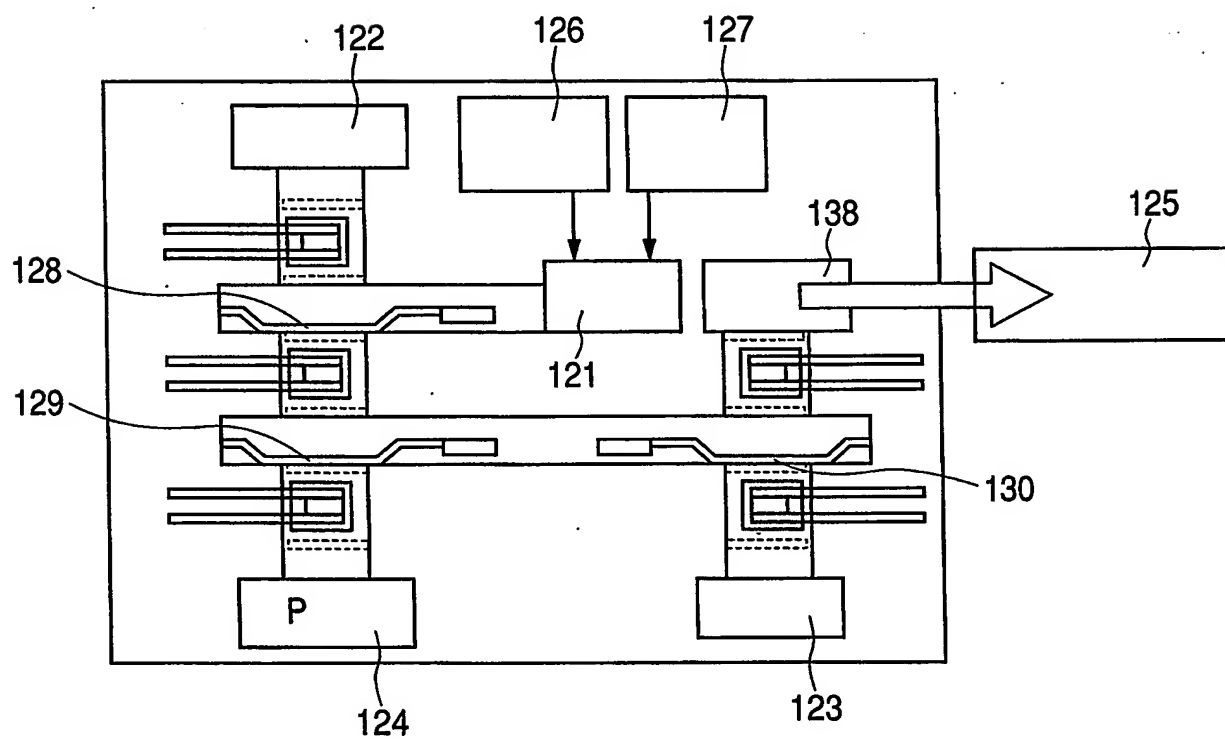
*FIG. 11A*



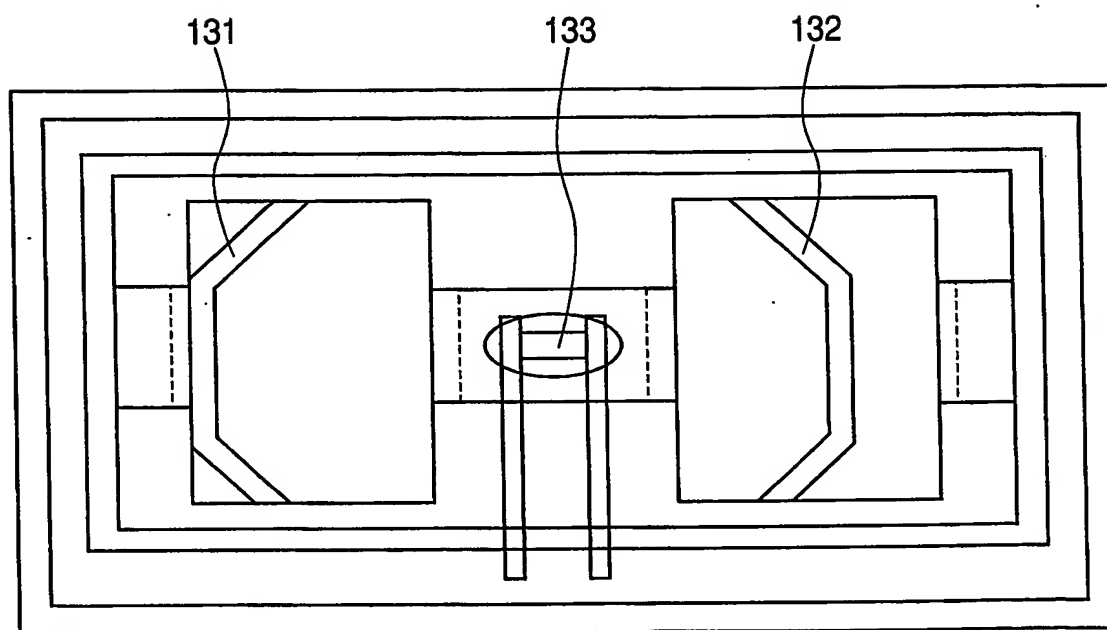
*FIG. 11B*



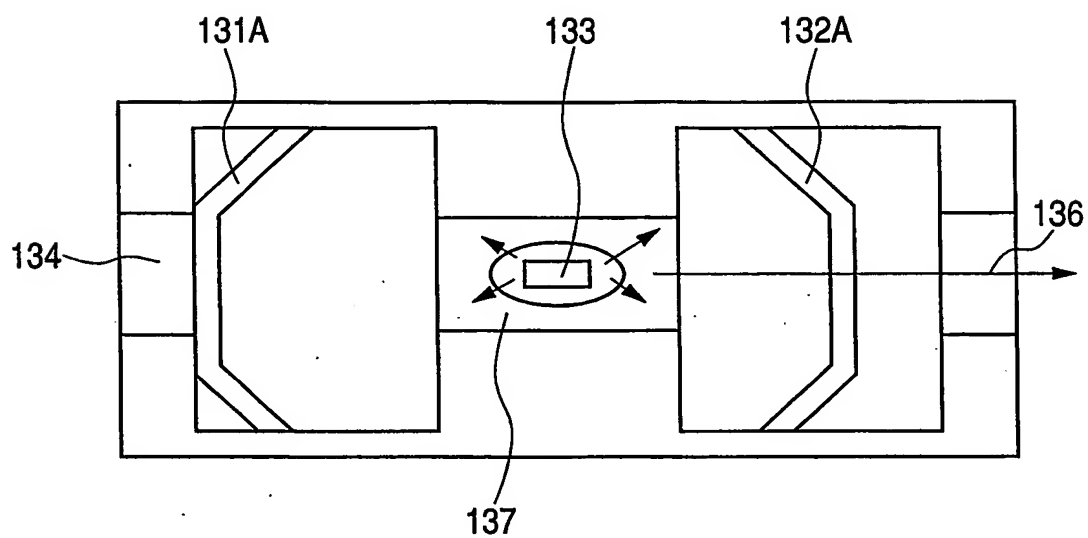
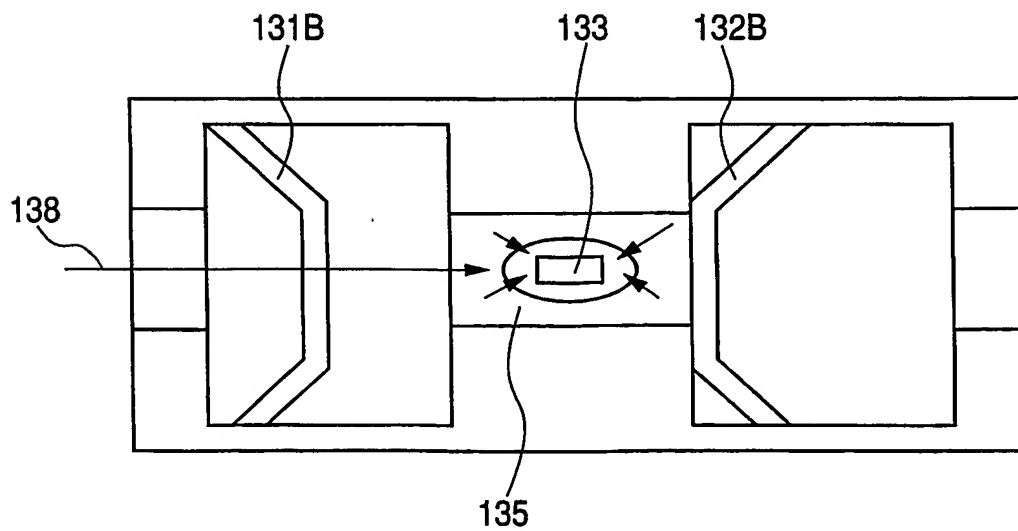
10 / 14

**FIG. 12**

*FIG. 13*

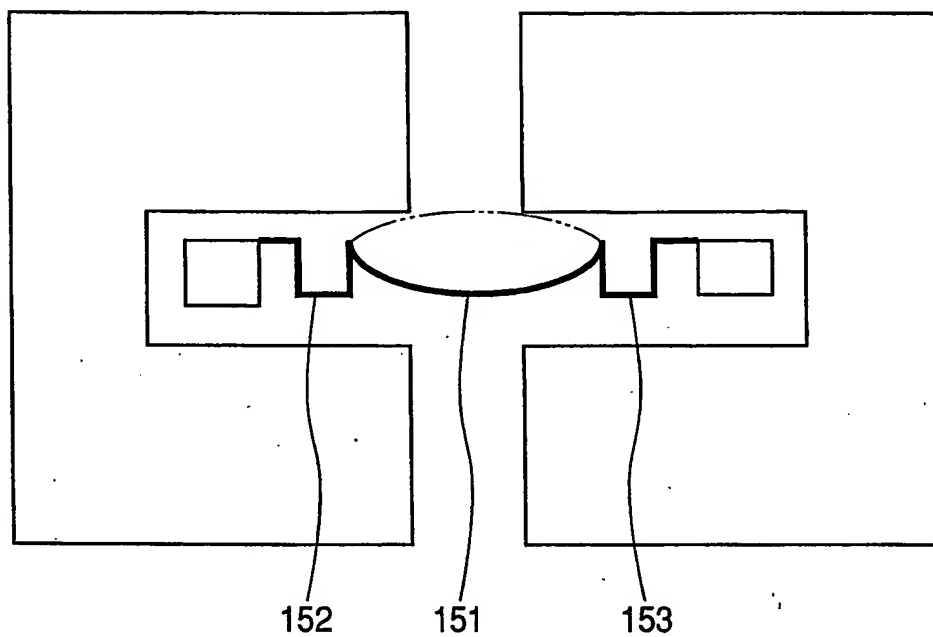


12 / 14

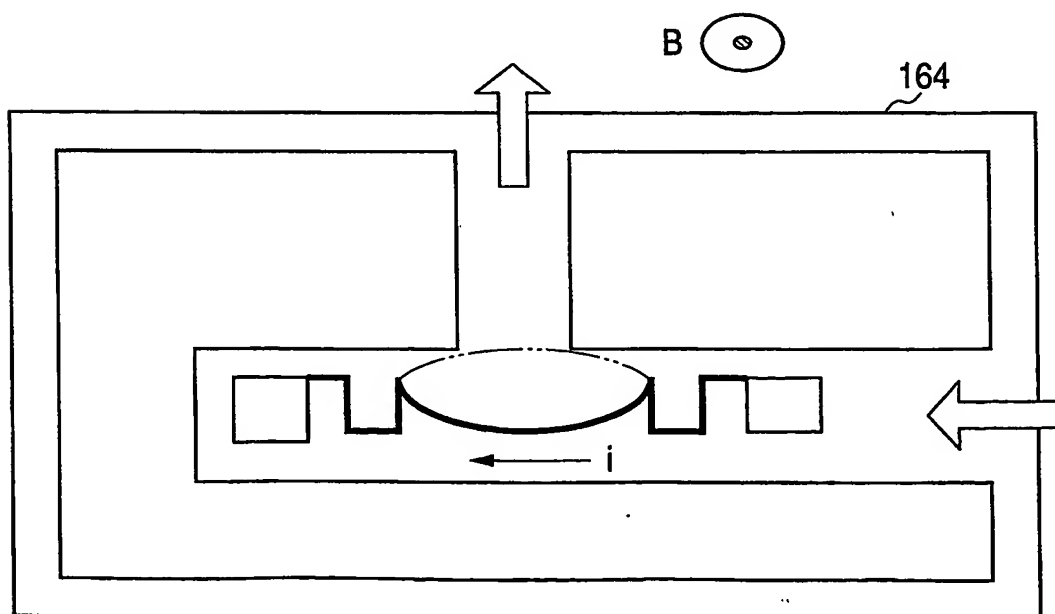
**FIG. 14A****FIG. 14B**

13 / 14

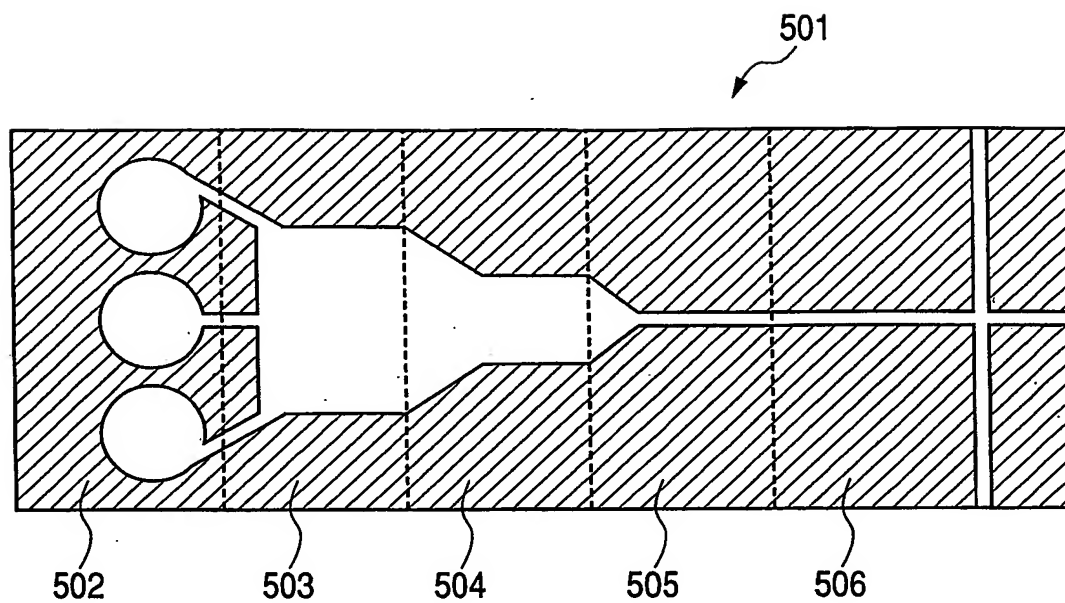
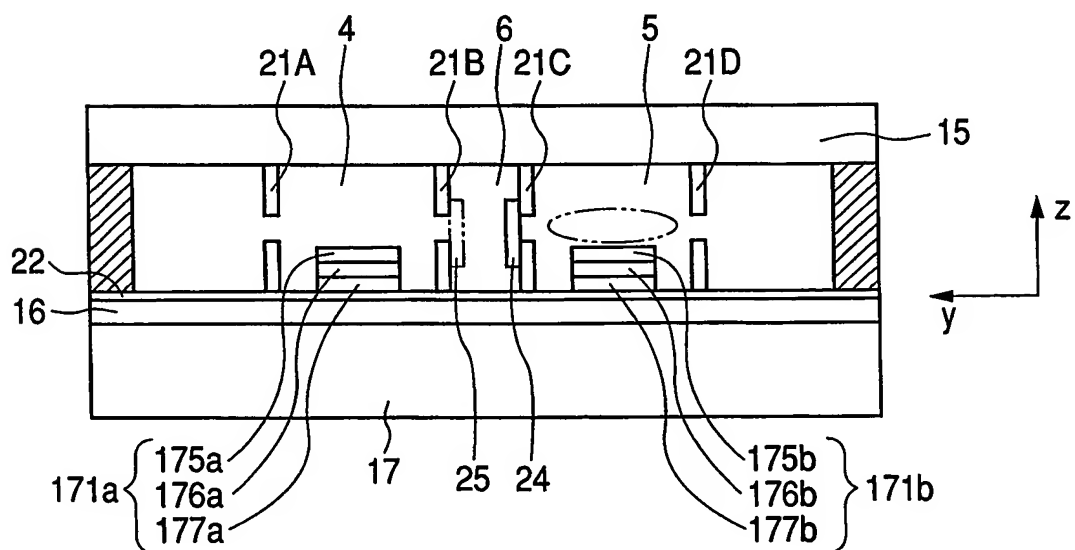
**FIG. 15**



**FIG. 16**



14 / 14

**FIG. 17****FIG. 18**

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/11429

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 F15C5/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 F15C F16K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EP0-Internal, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2 893 416 A (HEGSTAD LESTER O) 7 July 1959 (1959-07-07) column 2, line 23 -column 3, line 22 column 4, line 45 -column 58; figures 2-5,7	1,6,10
Y		2,4,5, 7-9
X	US 3 082 748 A (VOGEL ARTHUR C) 26 March 1963 (1963-03-26) column 1, line 40-44 column 2, line 65 -column 3, line 29; figures 1-3	1
X	US 3 112 768 A (THOMPSON RICHARD G) 3 December 1963 (1963-12-03) the whole document	1
	-/--	



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

27 November 2003

Date of mailing of the international search report

09/12/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Busto, M

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 03/11429

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 768 521 A (BRYCHTA O ET AL) 30 October 1973 (1973-10-30) column 2, line 38 -column 3, line 53; figure 1	1
Y		2
A	WO 02 33268 A (UNIV NEW YORK) 25 April 2002 (2002-04-25) abstract; figure 1	1
Y		4
A	US 6 131 880 A (FUCHS HEINZ ET AL) 17 October 2000 (2000-10-17) abstract; figure 1	1
Y		5
A	WO 02 40874 A (CHOU HOU PU ;QUAKE STEPHEN R (US); SCHERER AXEL (US); THORSEN TODD) 23 May 2002 (2002-05-23) abstract; figure 1	1
Y		7,8
A	US 6 283 440 B1 (EVANS JOHN) 4 September 2001 (2001-09-04) column 3, line 21-31; figure 2	1
Y		9

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 03/11429

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2893416	A	07-07-1959	NONE	
US 3082748	A	26-03-1963	NONE	
US 3112768	A	03-12-1963	NONE	
US 3768521	A	30-10-1973	BE 767661 A1 CA 933870 A1 CH 539210 A DE 2126165 A1 FR 2090307 A5 GB 1323887 A	18-10-1971 18-09-1973 15-07-1973 09-12-1971 14-01-1972 18-07-1973
WO 0233268	A	25-04-2002	AU 1340002 A WO 0233268 A2 US 2002043638 A1	29-04-2002 25-04-2002 18-04-2002
US 6131880	A	17-10-2000	DE 19523915 A1 BR 9606453 A CN 1157030 A WO 9702433 A1 DE 59610001 D1 EP 0778924 A1 JP 10505403 T US 5924674 A	02-01-1997 23-12-1997 13-08-1997 23-01-1997 30-01-2003 18-06-1997 26-05-1998 20-07-1999
WO 0240874	A	23-05-2002	AU 3052402 A EP 1343973 A1 WO 0240874 A1	27-05-2002 17-09-2003 23-05-2002
US 6283440	B1	04-09-2001	AU 1925600 A WO 0032972 A1	19-06-2000 08-06-2000